

Physics of the Debye temperature

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Textbooks introduce the Debye temperature to simplify the integration of the heat capacity. This approach gives the impression that the Debye temperature is a parameter which makes the integration more convenient. The Debye temperature separates the independent and the interacting thermal lattice vibration which should be clearly explained to students. An example of such explanation, deriving the Debye temperature from basic quantum and thermodynamic assumptions, is presented. The equations derived from theory are tested by experiments of face-centered cubic structures. Correlation between the minimum acoustic wavelength and the mean acoustic velocity is detected.

I. INTRODUCTION

In solid phase, by assuming small displacement from the equilibrium position, atoms execute simple vibrational motion in the x, y, and z direction which is called lattice vibration. Assuming linear elasticity the internal energy of a system [U] can be calculated as:

$$U = \sum_{i=1}^N \sum_{\alpha=1}^3 \left(\frac{p_{i\alpha}^2}{2m_i} + \frac{1}{2} \kappa_i \xi_{i\alpha}^2 \right) \quad (1)$$

where $\alpha = 1, 2, \text{ or } 3$, p is the momentum of the particle, m is the mass of the particle, κ is the force constant, and N is the number of the vibrating units. The variable ξ is defined as:

$$\xi_{i\alpha} \equiv x_{i\alpha} - x_{i\alpha}^{(0)} \quad (2)$$

where $x^{(0)}$ is the equilibrium position of the particle¹. If the temperature is high enough then classical physics is applicable and Eq.(1) can be used to determine the internal energy of the system. Applying the equipartition theory gives the internal energy

$$U = 3N \left[\left(\frac{1}{2} \right) k_B T \times 2 \right] = 3n N_A k_B T = 3nRT, \quad (3)$$

where k_B is the Boltzmann constant, T is the absolute temperature, R is the universal gas constant, n is the number of mols and N_A is the Avogadro number. The molar heat capacity at constant volume $[c_v]$ is

$$c_v = \frac{1}{n} \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} (3N_A k_B T) = 3R = 24.94 \text{ J/mol}. \quad (4)$$

This theoretical value of the molar volume heat capacity is known as the DuLong-Petit law². At room temperatures Eq. (4) is in excellent agreement with experiments; however, at low temperatures significant deviation is observed. Einstein proposed that the independent harmonic vibration of the atoms around their equilibrium position must be quantized³ in accordance with Planck's suggestion^{4,5}. According to quantum mechanics the possible energy levels of a harmonic oscillator are

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad n = 0, 1, 2, \dots \quad (5)$$

where n is the quantum number, \hbar is the Planck's constant divided by 2π , and ω is the angular frequency in radians. Assuming that in solid phase all atoms vibrate with the same frequency the total energy is then

$$U = 3nN_A \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \right). \quad (6)$$

The molar heat capacity at constant volume is

$$c_v = \frac{1}{n} \left(\frac{\partial U}{\partial T} \right)_v = - \frac{3N_A \hbar \omega}{k_B T^2} \left[- \frac{\hbar \omega e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2} \right]. \quad (7)$$

Introducing the characteristic Einstein temperature θ_E

$$\theta_E \equiv \frac{\hbar \omega}{k_B}. \quad (8)$$

Eq. (7) can be written as:

$$c_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1 \right)^2}. \quad (9)$$

Both the Dulong-Petit and Einstein models assume independent atomic vibration. Born and Von Karman⁶ proposed that the bonding in solid phase prevents independent atomic vibration and that the vibration should be collective lattice oscillation. If the particles are interacting then the potential energy of the particle in the crystal depends on the distance from its neighbor and Eq.(1) must be modified as:

$$U = \sum_{i=1}^N \sum_{\alpha=1}^3 \frac{p_{i\alpha}^2}{2m_i} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^3 \sum_{\alpha=1}^3 \kappa_{ij} (\xi_{i\alpha} - \xi_{j\alpha})^2 \quad (10)$$

The three dimensional bonding interactions are complex. In order to overcome on the complexities Debye simplified the problem⁷ by assuming that the velocity of the sound in solid $[v_s]$ is constant for all the frequencies leading to $\sigma_D(\omega) \propto \omega^2$. The spectral distribution then can

be defined as:

$$\sigma_D(\omega) \begin{cases} \sigma_c(\omega) & \text{for } \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad (11)$$

where ω_D is the Debye frequency. The distribution is terminated at the point when the number of vibration becomes equal with the number of degrees of freedom. Introducing the Debye function

$$f = 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (12)$$

and

$$x = \frac{\hbar\omega}{k_B T} \quad \text{and} \quad x_D = \frac{\hbar\omega_D}{k_B T} = \frac{T}{T_D} \quad (13)$$

where T_D the Debye temperature defined as:

$$T_D \equiv \frac{\hbar\omega_D}{k_B}. \quad (14)$$

The molar heat capacity at constant volume can be calculated as:

$$c_v = 3Rf = 9N_A k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (15)$$

Equation (15) has to be evaluated numerically⁸. The approximation of the Debye model is valid for all monoatomic solids.

The introduction of the Debye model is part of the standard curriculum in any solid state physics course^{9, 10} and has been covered from different aspects in this journal¹¹⁻¹⁶. Textbooks define the Debye temperature in the form of Eq. (14) as part of the integration of the heat capacity^{1,9, 10, 17}. This approach gives the impression that the Debye temperature is a parameter which makes the integration easier. The Debye temperature has very important physical meaning which should be clearly explained to students. An example of such explanation is presented.

II. THEORY

In solid phase the lattice vibrations are quantized and can be described by quasi-particles, phonons. It is assumed that the phonons represent a normal mode vibration thus all parts of the lattice vibrate with the same frequency. This quantum mechanical approach can be modeled as a particle in a box.

Assuming that the particle is in a cubic box and that the length of the box is L then the wavelength $[\lambda_n]$ of the phonon vibration is

$$\lambda_n = \frac{2L}{n} \quad (16)$$

where n is a positive integer. The frequency of the vibrating phonons $[v_n]$ can be determined from the speed of the sound inside the solid

$$v_n = \frac{v_m}{\lambda_n} = \frac{nv_m}{2L} \quad (17)$$

where $[v_m]$ represents the mean acoustic velocity calculated from the longitudinal $[v_p]$, and transverse $[v_s]$ sound velocities as:

$$v_m \equiv 3^{\frac{1}{3}} \left(\frac{2}{v_s^3} + \frac{1}{v_p^3} \right)^{-\frac{1}{3}} \quad (18)$$

The energy of the phonon is

$$E_n = hv_n \quad (19)$$

where h is a Planck's constant. Substituting Eq. (17) into Eq. (19) gives the energy of the phonon as:

$$E_n = hv_n = \frac{hv_m}{\lambda_n} = \frac{nhv_m}{2L} \quad (20)$$

In three dimensional spaces the phonon energy is the sum of its dimensional components

$$E_n = \sqrt{E_{nx}^2 + E_{ny}^2 + E_{nz}^2} = \sqrt{\left(\frac{hv_m}{2L} \right)^2 (n_x^2 + n_y^2 + n_z^2)} \quad (21)$$

The total energy of the sonic vibrating system is then

$$U = \sum_{n_x} \sum_{n_y} \sum_{n_z} E_n \bar{N}(E_n) \quad (22)$$

where $\bar{N}(E_n)$ is the number of phonons in the box with energy E_n .

The size of the vibrating units sets a limit on the minimum wavelength since shorter wavelengths do not lead to new modes of the vibration. This minimum wavelength sets a maximum frequency $[v_{\max}]$ and a highest mode number $[n_{\max}]$ that an acoustic vibration can reach. The maximum frequency limits the vibrational energy, and the highest energy of acoustic vibrations is

$$E_{\text{acoustic}}^{\max} = hv_{\max} = \frac{hv_m}{\lambda_{\min}} \quad (23)$$

If all the atoms in the system possess the maximum acoustic vibrational energy then the maximum energy which can be reached by acoustic thermal vibration is:

$$U_{\text{acoustic}}^{\max} = \sum_{n_x} \sum_{n_y} \sum_{n_z} n N_A E_{\text{acoustic}}^{\max} = 3n N_A E_{\text{acoustic}}^{\max} \quad (24)$$

Beyond this energy interacting or organized lattice vibration does not exist and the thermodynamic behavior of the system is described by independent lattice vibration. The internal energy of a system with independent thermal lattice vibration $[U_{\text{thermal}}]$ is given by Eq.

(3). The temperature where the acoustic vibration shifts to an independent thermal vibration is the Debye temperature, which can be defined as:

$$T = T_{\text{Debye}} \quad \text{when} \quad U_{\text{acoustic}}^{\text{max}} = U_{\text{thermal}} \quad (25)$$

Using the equality of the thermal internal energies Eq. (25) the Debye temperature can be expressed from Eqs. (23), (24), and (3) as:

$$T_{\text{Debye}} = \frac{h\nu_m}{k_B \lambda_{\text{min}}} . \quad (26)$$

This expression is identical with the conventional definition given in Eq. (14). Most text books use the symbol θ_D for the Debye temperature since the definition is introduced in relation to vibrational frequencies. I think the symbol T_D is more appropriate since it expresses clearly the temperature nature of the Debye temperature; therefore, this symbol will be used in the remaining part of this paper.

III. TESTING THE THEORY BY EXPERIMENTS

The simplest vibrating systems are monoatomic where the vibrating units are atoms. The size of these vibrating units can be represented by the atomic diameter $[d]$. Theoretically the acoustic lattice vibration (or interacting vibration) should start to vanish when half of the wavelength of the acoustic vibration reaches the atomic diameter, and should completely vanish when the wavelength of the acoustic vibration is equivalent to the atomic diameter

$$d \leq \lambda_{\text{min}} \leq 2d . \quad (27)$$

The minimum wavelength of the acoustic waves can be described as:

$$\lambda_{\text{min}} = ad . \quad (28)$$

where a is a numerical factor with a predicted value of

$$1 \leq a \leq 2 . \quad (29)$$

Assuming that the atoms are arranged in a closest packing arrangement gives the density of

$$\frac{\pi}{\sqrt{18}} \cong 0.74 . \quad (30)$$

Representing the atoms with equal spheres with radius of r the volume $[V]$ occupied by the atoms is

$$V = \frac{\sqrt{18}}{\pi} nN_A \frac{4\pi}{3} r^3 = 3.102 nN_A r^3 . \quad (31)$$

The radius of the atoms is then

$$r = \sqrt[3]{\frac{V}{3.102nN_A}} = 0.6857 \sqrt[3]{\frac{V}{nN_A}}. \quad (32)$$

Using the theoretical value for the minimum wavelength of the acoustic vibration Eq. (28), and substituting the radius of the atoms [Eq. (32)] into Eq. (26) gives the Debye temperature for closed packing atomic arrangements

$$T_D \approx \frac{h\nu_m}{k_B \lambda_{\min}} \approx \frac{h\nu_m}{2\pi k_B} = \frac{h\nu_m}{1.371395ak_B} \sqrt[3]{\frac{nN_A}{V}}. \quad (33)$$

Using the available acoustic velocity and Debye temperature data of elements with fcc structure¹⁸ (Ag, Au, Cu, Ni, Pb, Pt) the numerical factor [a] from Eq. (33) was calculated. Analyzing the data by plotting the calculated values of the numerical factor against the mean acoustic velocity reveals a linear correlation between these variables (Fig. 1). The correlation coefficient is 0.9977. The correlation can be described as:

$$a = 0.8692 + 1.6002 \times 10^{-4} \nu_m. \quad (34)$$

Substituting this correlation [Eq. (34)] into Eq. (33) gives the Debye temperature for fcc atomic arrangements:

$$T_D^{\text{fcc}} \approx \frac{h\nu_m}{adk_B} = \frac{h\nu_m}{1.371395(0.8692 + 1.6002 \times 10^{-4} \nu_m)k_B} \sqrt[3]{\frac{nN_A}{V}}. \quad (35)$$

The calculated Debye temperatures of Eq. (35) can reproduce the experimental values within 1%. The results are shown in table 1.

IV. CONCLUSIONS

In solid phase there are two kinds of lattice thermal vibrations, interacting and non-interacting. The temperature, which separates these different lattice thermal vibrations, is the Debye temperature. The general formula for the Debye temperature is derived from fundamental quantum and thermodynamic assumptions. Presenting this derivation to students helps to explain the physics behind this important thermodynamic parameter.

The derived expression of the Debye temperature was tested by experiments of monoatomic systems with fcc structure. The minimum wavelength of the acoustic vibration was assumed to be between d and 2d. The exact value of the numerical factor was calculated from the experiments. It has been found that the numerical factor correlates with the mean sound velocity. Using the detected correlation allows to reproduce the experimental values within 1%.

ACKNOWLEDGEMENTS

I would like to thank Alexandre Laugier for reading and commenting on the manuscript. This research was supported by Florida International University Graduate School Dissertation Year Fellowship.

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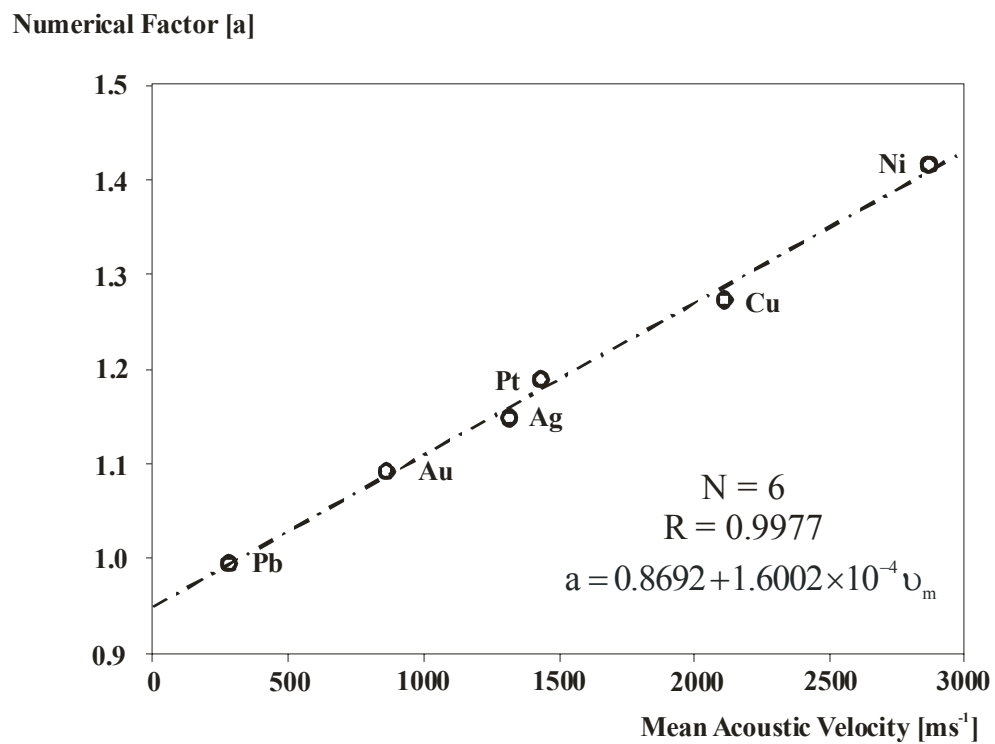


Fig. 1 Correlation between the numerical factor and the mean acoustic velocity.

Table 1.

Element	Transverse Sound Velocity [ms⁻¹]	Longitudinal Sound Velocity [ms⁻¹]	Mean Sound Velocity [ms⁻¹]	Molar Volume [cm³]	Debye Temperature [K]	Calculated Debye Temp. [K]	Difference [K]	Difference [%]
Ag	3650	1610	1817.4	10.27	215	213.0	-2.0	-0.9
Au	3240	1200	1362.2	10.21	170	170.7	0.7	0.4
Cu	4760	2325	2611.7	7.11	315	311.8	-3.2	-1.0
Ni	6040	3000	3366.7	6.59	375	376.9	1.9	0.5
Pb	1260	700	779.6	18.26	88	88.0	0.0	0.0
Pt	3260	1730	1933.4	9.09	230	232.3	2.3	1.0